

Ultrafast laser direct writing and nanostructuring in transparent materials

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An overview of recent achievements in the field of femtosecond laser writing in transparent materials is presented. Thanks to the unique properties of light-matter interaction on the ultrashort time scale, this direct writing technique has led to observation of unique phenomena, including nonreciprocal writing and anisotropic photosensitivity, in transparent materials and allowed engineering of novel photonic devices. © 2014 Optical Society of America

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1. Introduction

Material processing of transparent materials with lasers has become a fast growing field of research and technology. The very first investigations of laser-induced material modifications followed immediately after the invention of the laser in the early 1960s. Initially limited by studies of the unwanted damage caused by high laser fluences, this field sought the potential for controllable material processing. Further development of laser systems allowed focusing powerful high-quality laser beams into diffraction limited spots, leading to unprecedented optical intensities. As a result, the laser was able to serve as a unique and versatile contactless material modification tool.

The first lasers delivering subpicosecond pulses were demonstrated in the early 1970s with the advances in mode-locking techniques and organic dye lasers. However, these laser sources lacked stability and power and thus were limited to applications in spectroscopy. The 1990s saw the revolution of ultrafast laser technology. The invention of new mode-locking mechanisms, namely, Kerr-lens mode locking [1] and semiconductor saturable absorber mirrors [2], allowed generation of stable pulse trains from solid-state laser systems, which gave stability and power scalability. Additionally, the broad gain bandwidth of Ti:sapphire crystal allowed pulse durations close to a single optical cycle [3]. These achievements combined with chirped pulse amplification [4] allowed achievement of intensities of more than 10^{13} W/cm² with commercially available femtosecond laser systems. At such intensities, any transparent material will be ionized, leading to nonequilibrium conditions and fast cooling rates, which results in a material phase different from the initial one. Comparative studies revealed that femtosecond laser pulses can produce modification in the bulk of the material without the collateral damage that is observed for pulses longer than a few picoseconds [5–7]. Additionally, due to nonlinear absorption, the modification induced by short pulses could be even smaller than the beam spot size, leading to subdiffraction-limited resolution [8]. Initial studies of femtosecond laser material modification were performed in 1987 on the surface of polymethyl methacrylate (PMMA) with ultrafast excimer UV lasers [9,10]. Later, ablation of silica [11] and silver surfaces [12] was demonstrated using infrared femtosecond laser systems. This was followed by first demonstrations of femtosecond laser processing in the bulk of transparent materials made by the Hirao group, which demonstrated waveguiding structures written inside of silica glass [13]. Femtosecond-laser-induced refractive index modification was also applied for micromachining of laser amplifiers in Nd–, Er–Yb doped glasses [14,15] or Nd:YAG crystal [16]. The intrinsic nonlinear spatial confinement of femtosecond light pulses was applied to introduce polymerization into a resin [17]. This two-photon polymerization technique enabled printing 3D structures with a

30 nm resolution [18]. Development of new materials for photopolymerization allowed use of this technique for applications ranging from photonics devices to tissue engineering [19]. The virtues of short light pulses were also explored for modification of biological samples. The femtosecond laser pulses were used for dissection of chromosomes within the nucleus of a living cell [20] and for investigation of the neuronal network in the roundworm *C. elegans* [21].

2. Ultrafast Laser Systems

The laser system is the most important part of the laser direct writing setup. Initial experiments on femtosecond laser writing were performed predominantly with amplified Ti:sapphire laser systems. However, these laser systems had some drawbacks. First of all, the short lifetime of the upper state requires high intensity of the pump, and, as a result, such lasers are pumped by external lasers (for instance, frequency-doubled Nd:YAG). This leads to an increased footprint and complexity of the whole system, restricting the use of such systems to research-based activities. Additionally, only two configurations of amplified laser are available: low repetition rate (1 kHz) and high repetition rate (100 kHz). Recently, new laser systems with larger flexibility and higher stability have started replacing Ti:sapphire laser systems. Several different femtosecond laser systems based on crystalline gain media with rare-earth-ion doping (Nd^{3+} , Yb^{3+} , Er^{3+} , Tm^{3+} , Ho^{3+}) have been developed [22]. Despite a narrower gain bandwidth and, thus, potentially longer pulse durations, these gain media can be directly pumped by laser diodes offering high efficiency and stability in relatively compact packaging. The commercially available systems based, for instance, on a Yb:KGW crystal can deliver tens of watts of average power with a variable repetition rate and pulse energies of several hundred microjoules. The typical pulse duration for such amplified systems is in the range of several hundred femtoseconds, which normally is perfectly suitable for material processing. Another alternative to Ti:sapphire systems is fiber lasers, which can be even further reduced in size. The large surface area of the gain medium, i.e., the fiber, enables easy management of excess heat. Consequently, stable laser operation can be achieved with exclusively air cooling. The typical pulse energies of femtosecond fiber lasers are of several microjoules, which is sufficient for most of ultrafast laser writing tasks. Fiber lasers, however, are limited by the available peak power and normally operate at repetition rates above 1 MHz. At such high repetition rates, the femtosecond material processing is strongly influenced by heat accumulation [23,24]. However, fiber systems, such as the μ Jewel Family from IMRA, can now operate at repetition rates as low as 100 kHz, partially solving this problem.

3. Permanent Transparent Material Modification

The bandgaps of transparent materials (mostly dielectrics) are typically much larger than the energy of a single photon of the infrared laser source. For comparison, the bandgap of fused silica is about 9 eV, while the photon energy at 1030 nm wavelength is 1.2 eV. In the linear interaction regime, a photon with such energy $\hbar\omega$ is much smaller than the bandgap of the material E_g and thus cannot be absorbed. If, however, the light intensity is sufficiently high, nonlinear processes can lead to strong material ionization. There are two classes of such processes: nonlinear photoionization and avalanche ionization [25].

Photoionization refers to direct electron excitation by an electric laser field. This process can trigger initial seed electrons that are later heated up by inverse bremsstrahlung and start to participate in avalanche ionization. Depending on laser frequency and laser intensity, the ionization can occur in the form of tunneling or multiphoton absorption. Normally, the character of the nonlinear photoionization is evaluated by calculating the adiabatic parameter γ , also widely referred to as the Keldysh parameter [26]:

$$\gamma = \frac{\omega}{e} \sqrt{\frac{m_e c n_0 \epsilon_0 E_g}{I}}.$$

When the Keldysh parameter is smaller than 1.5, the tunneling process dominates the photoionization; if it exceeds 1.5, then the multiphoton process is dominant. In the multiphoton absorption regime, photoionization rate $P_{PI}(I)$ depends strongly on the laser intensity:

$$P_{PI}(I) = \sigma_k I^k,$$

where σ_k is the multiphoton absorption coefficient for k -photon absorption. The electron will be excited to the conduction band if the following condition is met:

$$k\hbar\omega \geq E_g.$$

The strong dependence on the intensity also means that the photoionization process is more efficient for short pulses. If the laser pulse gets sufficiently long, the photoionization process cannot efficiently supply the seed electrons and the excitation process becomes strongly dependent on random impurities with energy levels that lie close to the conduction band. As a result, the modification process becomes less deterministic.

Avalanche ionization involves free-carrier absorption followed by impact ionization [27,28]. The electrons already present in the conduction band oscillate in the electromagnetic field of the laser and gradually gain net energy by collisions. After the electron energy exceeds that of the bandgap, it can ionize, via collision, another electron from the valence band, resulting in two electrons near the bottom of the conduction band. Both electrons can again absorb energy and repeat the described energy transfer cycle. The process will continue as long as the light electric field is present. The density of electrons generated through the avalanche process is

$$\eta_{av}(t) = \eta_0 2^{w_{imp} t} = \eta_0 e^{w_{imp} t \ln 2},$$

where η_0 is the initial (seed) electron concentration and w_{imp} is the probability of impact ionization. One can see that avalanche ionization requires the presence of seed electrons, which triggers the process and is more efficient with longer pulse durations. The source of the seed electrons η_0 depends on the material. For material with defects or some dopants, initial electrons can be excited from these low-lying levels via linear absorption or thermal excitation [27]. For pure dielectrics, seed electrons are supplied via photoionization (for ultrashort pulses).

When a sufficient amount of energy is absorbed via the described mechanisms and is deposited into the material via electron–phonon coupling and defect formation, permanent damage occurs. There is, however, no widely accepted definition of damage threshold. Frequently, the damage threshold is characterized

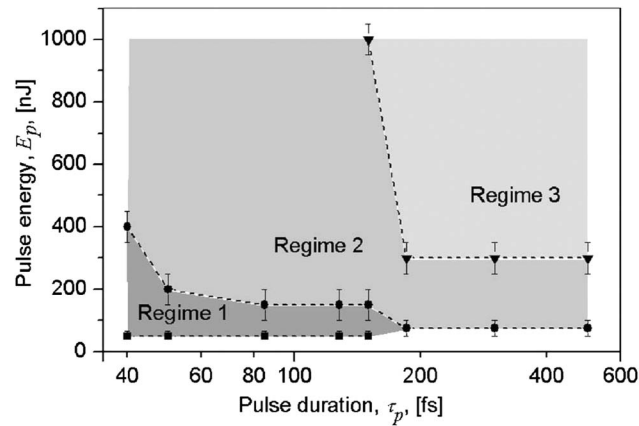
by *post mortem* optical measurements [27,29], considering the surface and bulk of the material are of the same quantity. However, these two situations are quite different. First of all, the laser focus at the surface is not affected by self-focusing and spherical aberration as is the bulk [30]. Second, the damage threshold on the surface may greatly vary with its preparation (type of polishing, impurities) and quality [31].

The character and mechanism of material modification largely depends on the laser pulse duration. During laser irradiation, electric field energy is absorbed by the electrons, which are excited into the conduction band. The excited electrons distribute energy among themselves via carrier–carrier scattering (10–100 fs) and also by carrier–phonon scattering (>10 ps). The first process leads to fast energy redistribution among the excited carriers; the second transfers the energy to the lattice, equalizing the temperature of the electrons and the lattice. The typical time-scale for electron energy transfer to the lattice is of tens of picoseconds.

Thus, if the laser pulse duration is of the same scale, a substantial amount of energy will be transferred to the lattice during pulse propagation [27]. The excited lattice phonons are transferring energy into the vicinity of the laser focus by thermal diffusion. Later, the material is permanently damaged if the temperature in the affected zone becomes sufficient to melt it. As a result, a strong tension gradient occurs, which leads to fracturing of the material, degrading the quality of the machined material. The damage threshold is then determined by a relative rate of energy deposition and thermal diffusion. It is known that the damage threshold (given in fluence) scales as the square root of the pulse duration. However, with the development of ultrafast lasers, a deviation from this law was observed with laser pulses shorter than 10 ps [29]. As was mentioned above, the damage threshold is measured mostly for the surface in order to avoid complications related to nonlinear effects, such as self-focusing, dispersion, and self-phase modulation. The deviation from the square root law can be explained by a rapid electron ionization mechanism. For pulses <10 ps, thermal diffusion and electron–ion interaction take place after the laser pulse; thus, the electrons can reach high temperatures, while keeping the lattice in the cold state during laser pulse irradiation. Afterward, the electrons release energy only to the irradiated zone, reducing the heat-affected zone and collateral damage in the vicinity. The permanent damage is typically related to the critical plasma concentration, when the laser irradiation is strongly absorbed by the excited electron plasma. However, recent direct measurements of the plasma concentration put this assumption under dispute. It was found that permanent damage can be induced even at subcritical plasma concentration [32,33].

Depending on the fluence, femtosecond laser irradiation can produce three types of modification in the bulk of fused silica: isotropic refractive index increase (Type 1) [13], nanogratings (Type 2) [34], and voids (Type 3) [7]. These three types can be clearly distinguished only for laser pulses shorter than about 200 fs [35,36] (Fig. 1). At longer pulses, nanogratings appear even at relatively low fluences, just above a permanent modification threshold. Extensive analysis of the thresholds of these modifications for silica doped with Ge, F, and P was presented by Poumellec *et al.* [37]. The threshold for Type 1 modification was independent of the doping and was 0.095 $\mu\text{J}/\text{pulse}$, whereas the threshold for nanograting formation was strongly affected by dopants and varied from 0.13 $\mu\text{J}/\text{pulse}$ for a 1.5% doped Ge:SiO₂ sample to 1.2 $\mu\text{J}/\text{pulse}$ for 0.3% F:SiO₂. For comparison, the threshold for pure silica was 0.31 $\mu\text{J}/\text{pulse}$.

Figure 1



Threshold pulse energies for different regimes of femtosecond-laser-induced modification in fused silica. Regime 1 corresponds to smooth refractive index modification. Regimes 2 and 3 correspond to nanograting formation. Reproduced with permission from Hnatovsky *et al.*, Appl. Phys. Lett. **87**, 014104 (2005) [35]. Copyright 2005, AIP Publishing LLC.

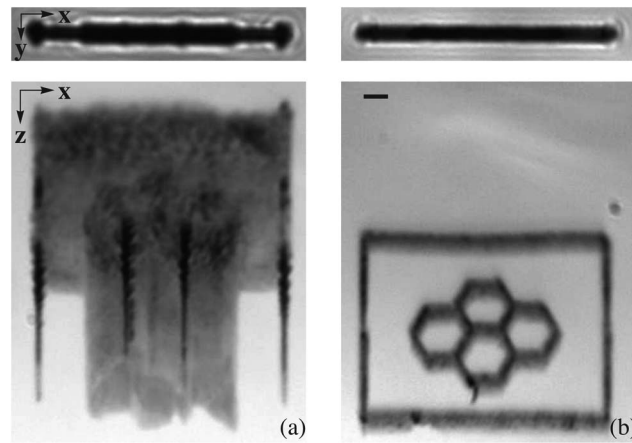
Another important parameter for femtosecond laser direct writing is focusing conditions, which roughly can be arranged into three groups depending on the numerical aperture (NA). The low NA regime is related to lenses with $NA < 0.1$; this gives a spot size of more than $10\ \mu\text{m}$. A femtosecond laser beam weakly focused into the bulk of transparent material turns into filament below the damage threshold, preventing single-shot permanent structural modification [38,39]. As a result, low NA lenses are typically used for surface modification, where self-focusing is not playing a crucial role. Lenses with NAs from 0.1 to 0.5 can already induce a confined permanent modification inside a transparent material. At these NAs, spherical aberration can strongly affect the laser beam propagation. The refractive index of fused silica is higher than that of air by 0.5. The light is therefore nonuniformly refracted at the interface between the air and the material. As a result, the adjacent part of the beam is focused deeper than the central, thus extending the focal region in the direction of propagation. This also effectively reduces the angular spectrum of the focused laser beam, and the spot size becomes larger. The strength of this effect increases with NA. The refractive index mismatch can be compensated by using objectives with spherical aberration correction, immersion optics, or adaptive optics methods (Fig. 2) [40,41].

Even larger NAs ($NA > 0.9$) can be achieved with oil-immersion lenses. The immersion optics not only tightly focuses the laser beam but also compensates refractive index mismatch at the surface of the sample. As a result, a tightly focused femtosecond laser beam can modify material even at the nanojoule energy level [42,43]; i.e., an oscillator energy is sufficient to induce permanent modification.

3.1. Smooth Refractive Index Change

Smooth refractive index modification with femtosecond laser in the transparent material was first reported by Davis *et al.* [13]. The laser-written tracks exhibited positive refractive index change up to 0.035. Although the initial study did not

Figure 2

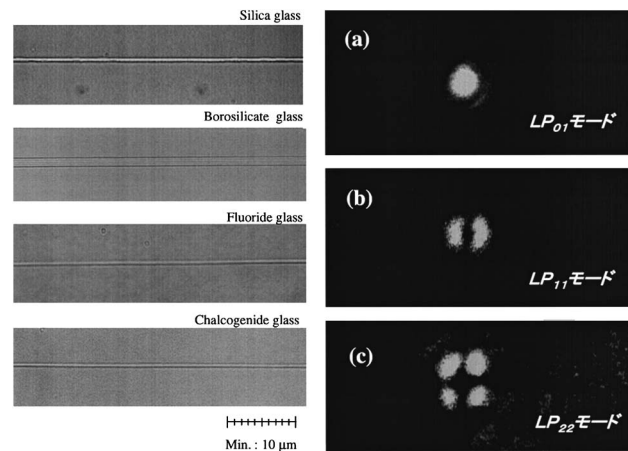


Femtosecond laser inscription (a) without and (b) with aberration correction using adaptive optics. Top (x - y) and side (x - z) view of a graphitic structure fabricated in diamond. The scale bar represents 5 μm . Reproduced with permission from Simmonds *et al.* [41]. Copyright 2011, Optical Society of America.

demonstrate light guiding in the laser-written tracks, following works confirmed the feasibility of writing relatively low-loss (<0.15 dB/cm) waveguides in silica glass [44,45] (Fig. 3).

Normally, refractive index modification with lasers requires photosensitivity of the glass, which can be induced by Ge doping [46]. The advantage of a femtosecond laser is that it does not require initial photosensitivity, thus enabling writing of waveguides in various types of material. Another advantage is the ability to induce refractive index change deep in the bulk of the material, allowing

Figure 3



(Left) Micrographs of femtosecond laser-written tracks in various glasses. (Right) Near-field patterns at 800 nm on fluoride glass waveguides where the core diameters are (a) 8 μm , (b) 17 μm , and (c) 25 μm . Reproduced with permission from Miura *et al.*, Appl. Phys. Lett. **71**, 3329–3331 (1997) [44]. Copyright 1997, AIP Publishing LLC.

complex geometries to be implemented. As a result, femtosecond-laser-written waveguides have found numerous practical applications in such fields as telecommunications [13,47], microfluidics [48], astronomy [49,50], and quantum optics [51–54].

The observed refractive index increase was explained by two models based on defect formation and material densification with the increase of fictive temperature.

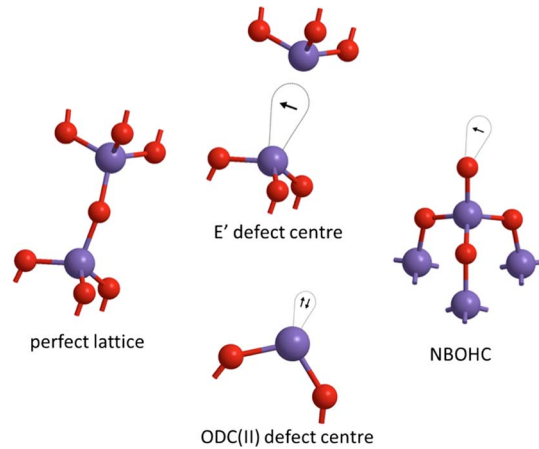
3.2. Defect Formation and Refractive Index Change

The first explanation is based on refractive index change through a Kramers–Kronig mechanism, where increased absorption due to photoinduced defects leads to increased refractive index [55]. Although defect formation under ultra-short laser irradiation is not yet fully understood, occurrences can be explained by relaxation of self-trapped excitons [56]. Self-trapped excitons can be formed as a result of free exciton self-trapping. Alternatively, a positive hole may be trapped on the distortion of the lattice and, after trapping, an electron forms a self-trapped exciton. The relaxation of excitons to defects occurs a few tens of picoseconds after laser excitation. The self-trapping process is accompanied by strong distortion of the SiO₂ lattice. Weakening of Si–O–Si bonds yields oxygen displacement from the equilibrium position, leading to formation of silicon and oxygen dangling bonds [56]. This is the main source of refractive index change induced with UV laser sources. Indeed, femtosecond laser pulses also induce two types of defect: oxygen-deficient or oxygen-excess [57,58], which exhibit characteristic absorption and photoluminescence bands. Examples of the optically active oxygen-deficiency-related defects are diamagnetic oxygen-deficiency centers, most commonly noted as ODC(II), and paramagnetic E' centers, where a silicon atom has one unpaired electron [57,59] (Fig. 4). The oxygen-excess defects most commonly found in fused silica are nonbridging oxygen hole centers (NBOHCs), which give rise to pronounced red luminescence with a peak at around 650 nm (1.9 eV) [60]. However, most of the defects can be annealed at 400°C, whereas the partial refractive index change remains up to 900°C [61]. Thus, defects can only partially explain the laser-induced refractive index increase.

The second explanation is based on rearrangement of the silica network as a result of fast temperature change in the irradiated zone. Raman studies confirmed that the irradiated zone contains an increased concentration of 3 and 4 member rings in the silica structure, which indicates densification [62]. Additionally, it is known that silica density increases with fictive temperature, which is the measure of order in glassy media and reflects the thermal history of the glass preparation [63]. The higher is the fictive temperature, the higher is the disorder of the matrix. For most glasses, a slow cooling rate leads to a state with higher density. However, pure silica glass exhibits an exception with the highest density observed at a fictive temperature of 1500°C [64]. The refractive index grows as the density of glass increases. Femtosecond laser pulses lead to an increase of fictive temperature in the irradiated region, locally modifying the refractive index.

Additionally, glass matrix rearrangement is caused by shock waves [65–67]. Some glasses, such as borosilicate or soda-lime, or crystalline materials exhibit refractive index decrease over the entire femtosecond-laser-irradiated zone.

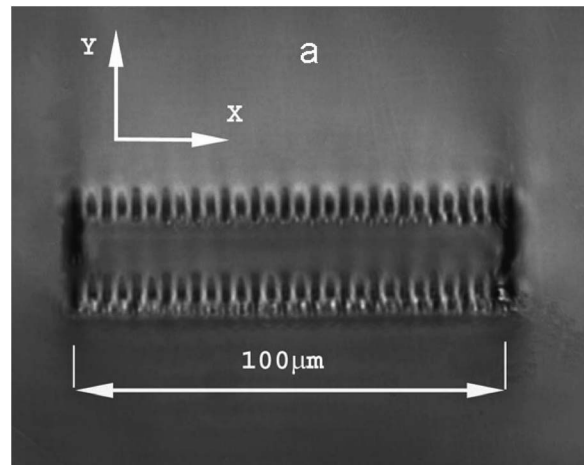
Figure 4



Structural models of perfect SiO₂ lattice and most-abundant laser-induced defects. Purple spheres, silicon; red, oxygen. Oxygen deficiency centers: E' , asymmetrically relaxed oxygen vacancy with an unpaired electron localized in a sp^3 -like orbital of a single Si atom; ODC(II), divalent Si atom. Oxygen excess center: NBOHC, oxygen dangling bond. Based on [59,60].

However, waveguiding structures still can be produced in these materials by stress. The expanding material in the irradiated zone induces strain in the vicinity of the track, and as a result the refractive index increases. Waveguiding structures can be induced between two or more adjacent laser tracks (Fig. 5). This technique was successfully applied for the fabrication of waveguide lasers in doped glasses and crystals [15,16,68].

Figure 5



Cross section of a depressed cladding waveguide inscribed in YAG:Nd³⁺. Multiple laser-written tracks create a stress zone with a refractive index increase, where light can be guided. Reproduced with permission from Okhrimchuk *et al.* [16]. Copyright 2005, Optical Society of America.

3.3. Waveguide Writing Techniques

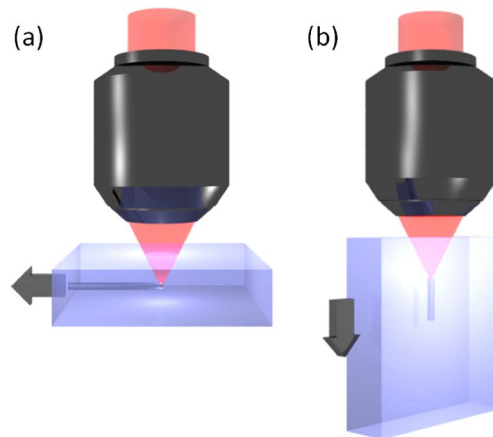
Integrated optical devices are fabricated by scanning with a femtosecond laser beam through the glass structure in order to create a continuous densified zone. Typically, the laser beam is stationary, and a translation stage is used to displace the sample. The writing process can be made either by translating longitudinally or transversely with respect to the laser beam propagation direction (Fig. 6).

The advantage of longitudinal writing geometry is that the resulting waveguiding structures have symmetric cylindrical cross sections. However, the writing depth is limited by the working distance of the focusing lens and spherical aberrations, which distort the focus. The waveguides can thus be only a few millimeters long. Additionally, such an approach allows fabrication of only straight waveguides. Waveguides can also be written at loose focusing and high peak powers, resulting in self-focusing and filamentation [69]. The diameter of filament-induced permanent refractive index change is smaller than $2\text{ }\mu\text{m}$. The lengths of imprinted tracks can vary from 20 to $500\text{ }\mu\text{m}$, depending on the NA of the focusing lens, and refractive index change was 0.8×10^{-2} .

In the transverse geometry, the waveguide length is no longer restricted by the working distance of the lens. This writing scheme also allows implementation of more complex structures, such as bended waveguides and Y splitters [47,70,71]. The disadvantage of transverse scanning is the characteristic cross section of an asymmetric droplet shape [72]. The reason for this asymmetry is that for a Gaussian beam, the depth of focus ($2z_r$) is larger than the spot size ($2w_0$) by a factor $2z_r/2w_0 = n/\text{NA}$, where n is the refractive index of the medium and NA is the numerical aperture of the lens. As the refractive index of fused silica is around 1.45, the asymmetry vanishes only if expensive and short-working-distance oil-immersion objectives are used.

The symmetry can be achieved by multiple laser scanning and inducing a waveguide with an almost step index profile [45,73]. As the same sample volume is irradiated multiple times, sufficient refractive index change can be achieved by lower peak power, resulting in a lower concentration of scattering and

Figure 6



(a) Transverse and (b) longitudinal writing geometries for femtosecond laser waveguide fabrication in the bulk of transparent materials. The gray arrows indicate sample movement direction.

absorption defects. It is worth adding that this technique enables demonstration of laser-written waveguides with the lowest propagation losses (0.12 dB/cm) [45]. However, this comes at the cost of prolonged fabrication.

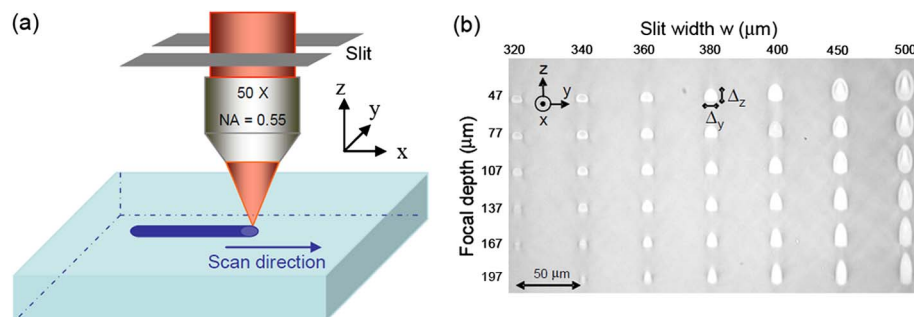
Alternative solutions to the waveguide asymmetry problem were suggested by several groups. The basic idea is to premodify the laser beam in such a way that depth of focus and spot size would be of the same size. Beam reshaping was achieved by controlling the amplitude or phase of the incident beam. The first system proposed to solve the asymmetry problem was a set of two cylindrical lenses, which introduced and controlled the astigmatism of the laser beam. The symmetry of the waveguide could be controlled by the position of the second cylindrical lens [74].

A symmetrical cross section can also be achieved with a much simpler system, which consists of just one slit (Fig. 7). Initially this technique was demonstrated for laser fabrication of the microchannels but later was successfully applied to the waveguide writing [75]. The symmetry is maintained only along one axis and requires an additional tracking mechanism to inscribe complex-shaped waveguides. Recently, an adaptive slit beam shaping method was suggested, where a slit was replaced by a spatial light modulator (SLM) [76]. In this case, a slit is generated by a phase diffraction grating displayed on the SLM, which diffracts a narrow slit of light. The slit is then re-imaged on the objective by the $4f$ system. The adaptive optics not only allows control of the slit width during the writing process but also synchronously follows the direction of laser-written track by “rotating” a diffraction grating pattern on the SLM.

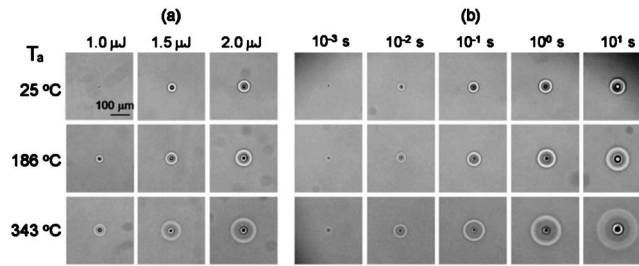
Another solution is to employ femtosecond lasers operating at hundreds of kilohertz or megahertz repetition rates. Typical examples of such systems are oscillator-only or fiber-based ultrafast laser systems, which can reach a tens of megahertz repetition rate. A train of laser pulses coming at a high repetition rate leads to heat accumulation and melting of the glass matrix (Fig. 8) [24,43,77]. The spherically symmetric heat-affected zone induced by the accumulated heat helps correct the asymmetry of the waveguides.

For fused silica, which has a high melting temperature, heat accumulation starts dominating above 1 MHz. For softer glasses, such as soda-lime, a strong temperature increase can be observed even at 200 kHz [78].

Figure 7



(a) Slit beam shaping setup. (b) Cross sections of laser-written waveguides in bismuth borate glass depending on slit width and focal depth. Reprinted from Yang *et al.* [70].

Figure 8

Optical microscope images of soda-lime glass modified regions after exposure to femtosecond laser pulses. In (a), the exposure time was kept constant (1 s) at different pulse energies. In (b), the material was irradiated with 2.0 μJ laser pulses with different exposure times. The ambient temperature is indicated on the left side. Reproduced with permission from Shimizu *et al.*, J. Appl. Phys. **108**, 073533 (2010) [78]. Copyright 2010, AIP Publishing LLC.

The heat-affected zone depends on the exposure time. It was recently demonstrated that the heat-affected zone can also be controlled by ambient temperature (Fig. 8). The modified area can be split into two regions: the inner modified region, where temperature exceeds the forming temperature of the glass, and the outer region, where the temperature is close to the glass transformation temperature. Thus, the mechanism of thermal modification includes not only melting but also softening of the glass.

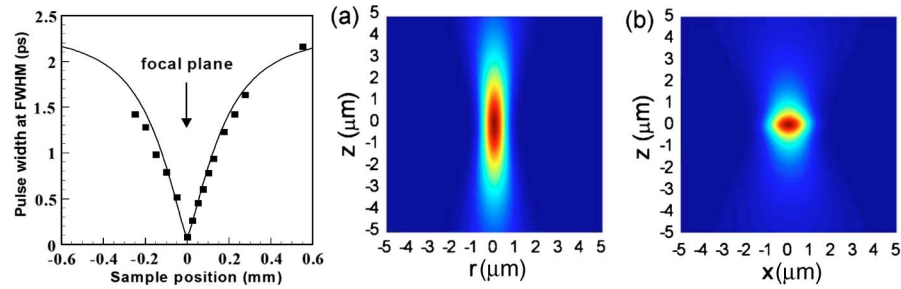
3.4. Spatiotemporal Focusing and Pulse Front Tilt

A focusing scheme based on the spatiotemporal properties of ultrashort pulses was recently suggested [79]. Initially, this technique was used for nonlinear microscopy as a way to remove unwanted background excitation. It is based on the fact that longer pulses exhibit a higher damage threshold due to lower intensity [80]. Stretching of the pulse is achieved by spatially chirping the femtosecond laser pulse using a pair of two prisms or a combination of a diffraction grating and a cylindrical lens [79]. The frequency components of the laser pulse are separated in space, and this effectively leads to a longer pulse duration. By focusing a spatially chirped pulse, different frequency components are brought together to produce the shortest pulse duration in the vicinity of the laser beam focus (Fig. 9). Such a focusing technique enables modification of material with loose focusing below the self-focusing threshold [81].

The spatiotemporal focusing was also found to be beneficial, inducing a symmetric cross section of the laser track (Fig. 9) [82]. The symmetric cross section obtained by this method can be achieved with NA of about 0.5. The low-NA objective together with spatiotemporal focusing still gives rise to asymmetry in the focus, which could be removed by adding a slit into the optical scheme [83].

Additional temporal control is required in the case of very short pulses spatiotemporally focused into material. The broad spectrum of the pulse becomes temporally distorted by the material's dispersion and must be corrected by adding temporal chirp using a pulse compressor. However, the combination of spatial and temporal chirp produces a pulse front tilt [84]. As a result of a pulse front tilt, the femtosecond laser beam exhibits directional dependence and anisotropic

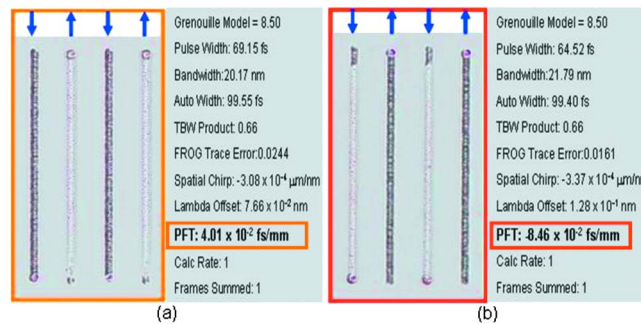
Figure 9



(Left) Measured (solid squares) and theoretically fitted (line) pulse width as a function of sample position. The location of the focal plane of the objective lens is set to be zero. Reproduced with permission from Zhu *et al.* [79]. Copyright 2005, Optical Society of America. (Right) Numerically calculated laser intensity distributions at the focus produced by an objective lens (a) without and (b) with a temporal focusing technique. Reproduced with permission from He *et al.* [82]. Copyright 2010, Optical Society of America.

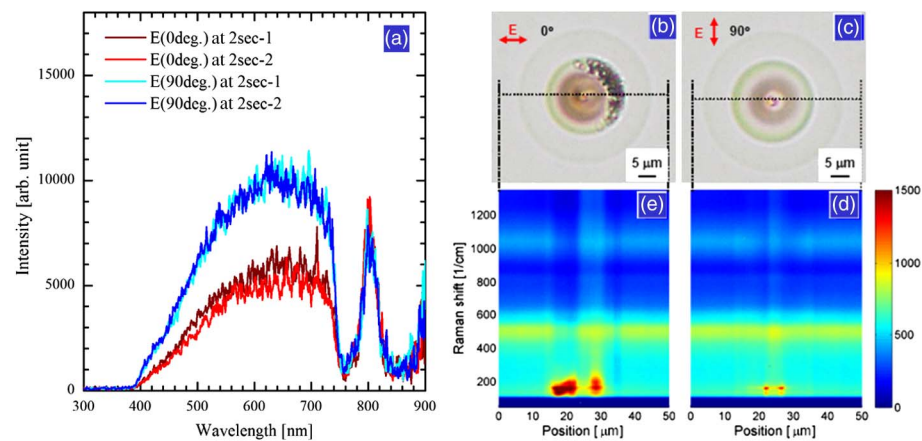
photosensitivity [85–87]. The pulse front tilt can also appear as a parasitic effect after the misaligned stretcher/compressor of a femtosecond laser. Even a small amount of pulse front tilt can lead to unexpected results, such as stronger modification and asymmetric bubble formation. Initially, the pulse front tilt was observed to cause a directional dependence in femtosecond laser direct writing experiments in fused silica [85]. Despite the symmetry of the laser beam with a Gaussian profile, the properties of the laser-inscribed tracks depended on the writing direction. The strongest directional dependence was observed at about 0.8–0.9 μJ . Birefringence was observed only for one writing direction. When the laser beam was rotated 90° by a two-mirror periscope, only weak directional dependence could be observed for the same set of experimental parameters. Later, it was demonstrated that the change of the pulse front tilt sign reversed directional dependence (Fig. 10) [88].

Figure 10



Microscope bright-field image of the line structures written using femtosecond pulses with (a) positive pulse front tilt or (b) negative pulse front tilt. The distance between the lines is 25 μm . The writing direction is shown by the arrows. The respective screen shots containing laser pulse parameters measured by a GRENOUILLE (grating-eliminated no-nonsense observation of ultrafast incident laser light e-fields) device are shown. Reprinted from Yang *et al.*, Appl. Phys. Lett. **93**, 171109 (2008) [88].

Figure 11



(a) Spectra of transmitted light during laser exposure with two orthogonal polarizations. The pump power at 800 nm was reduced by a factor of 105 using a notch filter. The results of two independent measurements for each polarization display good reproducibility. (b), (c) Transmitted light optical microscope images of modified regions irradiated for 1 s with two orthogonal polarizations. (d), (e) Corresponding Raman spectra along line scans through the irradiated regions. Reprinted from Kazansky *et al.* [87].

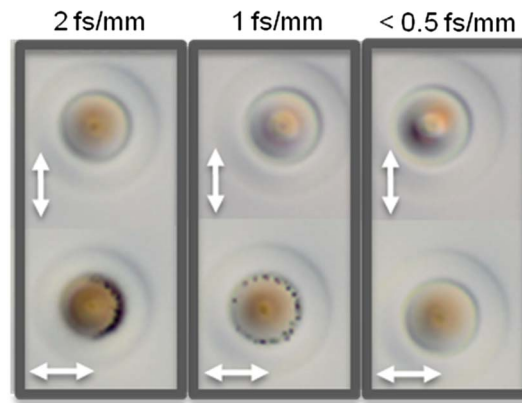
Another group demonstrated a setup that enables systematic control of pulse front tilt [86]. The proposed optical scheme allowed adjusting the magnitude of the pulse front tilt by changing the beam aspect ratio, i.e., the ratio of the spatially chirped beam dimension to the unchirped dimension. Although the focusing was performed by an off-axis parabola at much lower NA (0.03) than the previous work done by Yang and co-workers [85,88], a strong directional dependence was still observed in the bulk and on the surface of the material.

The pulse front tilt can also manifest in a stationary situation, i.e., when the sample is not moving with respect to the laser beam. It was demonstrated that the modification of glass depends on the mutual orientation of the light polarization azimuth and the pulse front tilt [87]. The experiments were performed in aluminosilicate (composition SiO_2 64, Al_2O_3 17, B_2O_3 5, CaO 15 wt. %) and silica glasses, indicating that the observed phenomenon does not depend on the material. In the experiment, a series of dots with different polarization orientations were printed into the glass. The intensity of the white light emitted during irradiation strongly depended on the laser beam polarization (Fig. 11). Raman spectroscopy and quantitative phase measurements showed a strong polarization effect in the structures permanently imprinted in aluminosilicate glass [Fig. 11(b)].

The strength of the polarization effect can be controlled by changing the pulse front tilt value (Fig. 12). For pulse front tilt < 0.5 fs/mm, the effect was almost negligible. The observed phenomenon was explained by ponderomotive force that arises due to temporal intensity anisotropy created by enhanced pulse front tilt in the vicinity of the focus.

An interesting result was recently demonstrated by Gecevičius *et al.* [89]. The polarization dependence of the laser-written structures depended on the interline distance. If the adjacent tracks did not overlap, the polarization dependence

Figure 12



Dots written with orthogonal polarizations and three different pulse front tilt values. As the pulse front tilt value decreases, the difference for two perpendicular polarizations becomes negligible. Reprinted from Kazansky *et al.* [87].

followed pulse front tilt. If, however, the tracks were overlapping, the laser-induced stress dominated in the polarization dependence.

The spatiotemporal characterization of the ultrashort pulses revealed the presence of a small pulse front tilt of about 1.8 fs/mm. Such an amount of pulse front tilt inevitably is present in almost any standard ultrafast laser system due to the chirped pulse amplification system. These small values can be significantly amplified in the vicinity of the focus. The numerical calculations predict a pulse front tilt of ~ 180 fs/mm 10 μm before the geometrical focus in air.

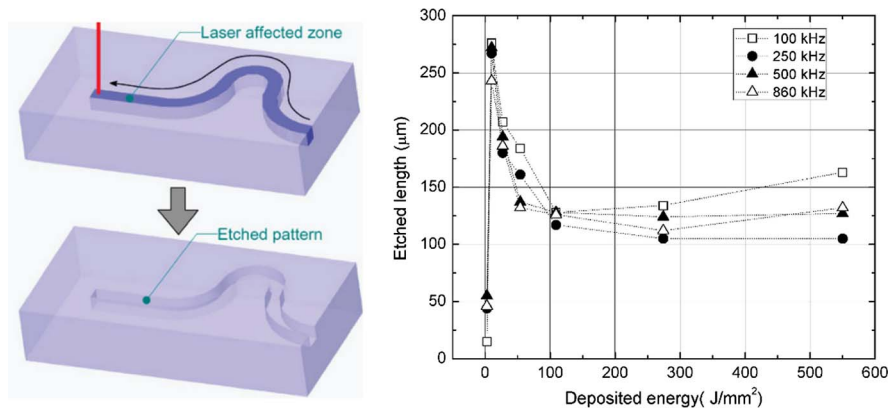
3.5. Femtosecond Laser Assisted Glass Etching

The femtosecond laser pulses also modify chemical properties of the glass. One of the most useful properties of this chemical modification is an increased etching rate of the irradiated region [90]. The light-modified silica glass matrix can be selectively etched by hydrofluoric acid of concentrations between 2.5% and 5% [91] (Fig. 13, left). The procedure can last several hours depending on the dimensions of the modified region. The etching rate is also strongly affected by the polarization of the writing laser beam [92,93].

The tracks written with polarization perpendicular to the writing direction are etched much faster than those written with parallel polarization. The explanation of this effect is still debated. At higher energies, the etching rate can be enhanced by the presence of nanocracks that are oriented perpendicular to the polarization. In this case, the transverse polarization should induce nanocracks oriented along the laser-inscribed track and assist in the penetration of the etchant. However, polarization-dependent etching was also observed at lower energies, below the nanostructure formation threshold [94], indicating that material densification and stress can also enhance the etching rate. Polarization-dependent absorption and the inner structure of the laser-written track can also contribute to the different etching rate.

A thorough analysis of the fabrication parameters revealed that the etching rate strongly depends on the amount of deposited energy [95]. The etching rate

Figure 13

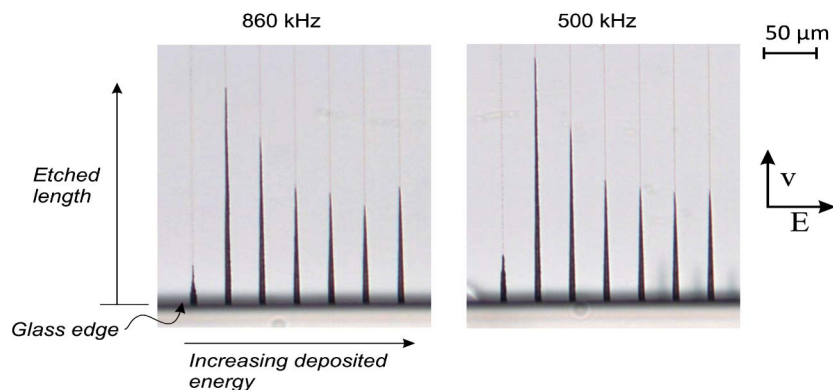


(Left) Illustration of the two-step microfabrication process of femtosecond laser assisted chemical etching of fused silica. Reproduced from Bellouard *et al.* [91]. (Right) Deposited energy versus etched length for various repetition rates as measured in an optical microscope. The laser polarization is transverse to the writing direction. The pulse energy E_p is 215 nJ. Reproduced with permission from Rajesh and Bellouard [95]. Copyright 2010, Optical Society of America.

response as a function of deposited energy presents two regimes (Fig. 14). The first is a sharp increase of the etching rate up to a maximum value, followed by a fast decrease of the etching rate to a certain value. Such behavior was observed for repetition rates from 100 to 860 kHz, indicating that it is not a cumulative effect.

The etching dependence was explained by the accumulation of stress, which grows with the number of pulses. The stress affects silica ring structures, leading to faster etching. The stress load increases rapidly on the apex of the structures to the point where material fails and cracks appear. After crack formation, the material relaxes and the etching rate drops.

Figure 14



Optical microscope image of partially etched channels written with femtosecond lasers at different repetition rates (500 and 860 kHz). In both cases, etching rate dependence on deposited energy is similar. Reproduced with permission from Rajesh and Bellouard [95]. Copyright 2010, Optical Society of America.

The laser etching technique was successfully implemented for fabrication of microfluidic channels, mechanical flexures, and as preforms for molds [96–98]. The combination of etching with refractive index modification even allows using ultrafast laser direct writing for lab-on-a-chip fabrication [48,99–102].

3.6. Self-Assembled Nanogratings

At higher laser fluences, smooth refractive index modification is replaced by self-organized structures. The first observation of laser-induced periodic structure formation dates back to the 1960s, when Birnbaum reported surface ripple formation on the surface of semiconductors [103]. Since then, ripple formation has been observed on virtually any material surface, including dielectrics, metals, and polymers. The phenomenon turned out to be rather universal; the ripples could be formed with wavelengths ranging from the mid-infrared to the blue end of the visible spectrum and from CW operation to femtosecond lasers. For normal incidence, the period of such structures is close to the wavelength of light and perpendicular to the laser beam's polarization [104]. For oblique incidence and TM polarization (electric field is in the plane of incidence), the ripples occur with one of two possible periods [105]:

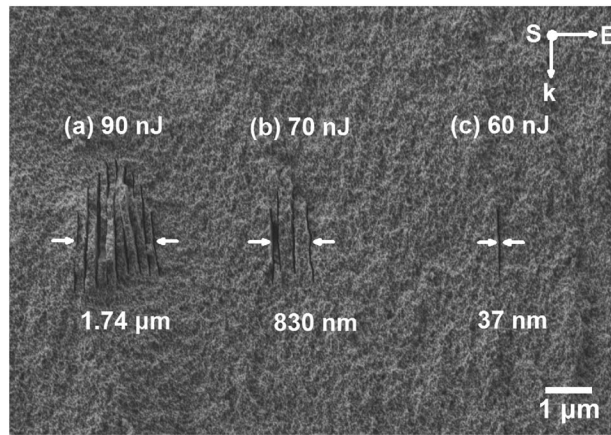
$$\Lambda_{\text{gr}} = \frac{\lambda}{1 \pm \sin \theta},$$

where θ is the angle of incidence and λ is wavelength of the incident laser light. For TE polarization, Λ_{gr} remains close to the wavelength λ . If the laser beam is moved with respect to the sample, the ripples can coherently extend over the scanned area [106].

However, ultrashort laser pulses were observed to induce two types of periodic surface structures [107]: above single pulse damage threshold—ripples with a period close to the wavelength—and below single pulse damage threshold—subwavelength ripples with periods as small as 30 nm [108]. The period was found to increase with the number of pulses and fluence [109]. Peculiarly, such structures could be formed only after tens or even thousands of laser pulses. A subwavelength period with sharp features cannot be explained by incident and scattered wave interference.

A decade ago, a new type of self-organization was observed inside SiO₂ glass after irradiation with an ultrafast laser [34,110], which was found to be responsible [111] for femtosecond-pulse-induced anisotropy and the propeller shape scattering reported earlier [112,113]. Under certain irradiation conditions, highly ordered subwavelength structures with features smaller than 20 nm could be formed in the irradiated volume. As opposed to surface ripples, nanostructures inside the material were found only for a handful of materials: fused silica, sapphire, and tellurium oxide [114,115]. Recently, Richter *et al.* observed nanograting formation in the bulk of ultralow expansion (ULE) and borosilicate glasses [116]. From this list, fused silica is the most common material for inducing nanogratings. Several studies on nanograting formation were conducted on modified silica glasses doped with germanium, phosphorus, or titanium. Nanogratings were also found in porous silica prepared from phase-separated alkali-borosilicate glass by removing the borate phase in the hot acid solution [117]. Even a single isolated nanoplane could be induced by controlling laser pulse energy, which can be used for writing nanofluidic channels (Fig. 15). Recently,

Figure 15

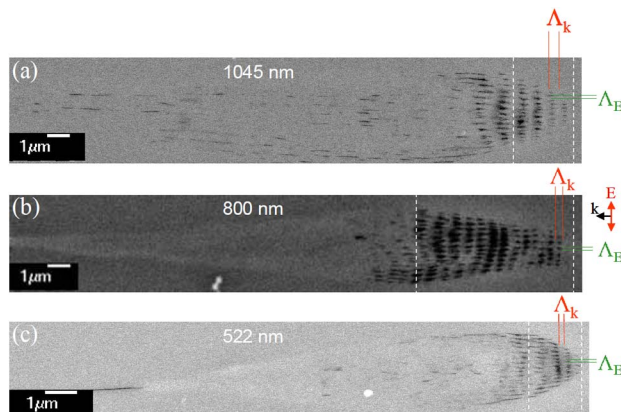


Nanograting formation dependence on the laser pulse energy. A single nanoplane was induced by 60 nJ laser pulses. Reproduced with permission from Liao *et al.* [117]. Copyright 2013, Optical Society of America.

volume nanogratings were reported to continuously transform into surface ripples when the laser focus was moved out of the sample [118].

Femtosecond-laser-induced nanogratings possess two periodicities: perpendicular to the polarization and along the light propagation direction [119] (Fig. 16). The first grating has a period smaller than the wavelength of light, in the range 100–300 nm, depending on the experimental conditions. The second period grows from the head of the structure to the tail with the initial period close to the light wavelength λ_0 in the material (refractive index n), i.e., λ_0/n . Recent studies suggest that the nanoplanes of the structure consist of a porous

Figure 16



Scanning electron microscope images of nanogratings formed by three different central wavelengths of the irradiated laser pulses. E, electric field of the writing laser; k , wave vector of the writing laser beam. (a) $\tau_p = 520$ fs, $E_p = 0.9$ μ J, writing speed 200 μ m/s, repetition rate 500 kHz. (b) $\tau_p = 150$ fs, $E_p = 0.5$ μ J, writing speed 100 μ m/s, repetition rate 250 kHz. (c) $\tau_p = 490$ fs, $E_p = 0.15$ μ J, writing speed 200 μ m/s, repetition rate 200 kHz. Reprinted from Yang *et al.* [119].

material [120], indicating possible glass decomposition during the irradiation of silica glass.

The theories suggested to explain nanograting formation are concentrated on explaining the subwavelength periodicity observed perpendicular to the light propagation direction. The first model proposed for volume nanograting formation was indeed an extension of traditional surface ripple formation theory [34] and relied on the interference of the bulk electron plasma longitudinal wave with the incident light. Coupling can occur only if the plasma wave propagates in the plane of light polarization. The initial coupling is presumably produced by inhomogeneities induced by electrons moving in the plane of light polarization. The periodic structure created due to the interference further enhances this coupling, resulting in periodic modulation of plasma concentration. Further, this modulation is frozen within the material. The nanograting period can be defined from conservation of the longitudinal component of momentum:

$$\mathbf{k}_{\text{ph}} + \mathbf{k}_{\text{gr}} = \mathbf{k}_{\text{pl}},$$

where $\mathbf{k}_{\text{ph}}$ is the photon wavevector, $\mathbf{k}_{\text{pl}} = \omega_{\text{pl}}/v_{\text{pl}}$ is the plasma wavevector, and $\mathbf{k}_{\text{gr}} = 2\pi/\Lambda_{\text{gr}}$ is the grating wavevector, with Λ_{gr} period. Explicitly the grating period can be written as

$$\Lambda_{\text{gr}} = \frac{2\pi}{\sqrt{\frac{1}{T_e} \left(\frac{m_e \omega^2}{3k_B} - \frac{e^2 \eta_e}{3\epsilon_0 k} \right) - k_{\text{ph}}^2}}.$$

This formula predicts an increase of the period with electron concentration η_e and temperature T_e . Steep increase of the period occurs when the electron concentration approaches the critical plasma density:

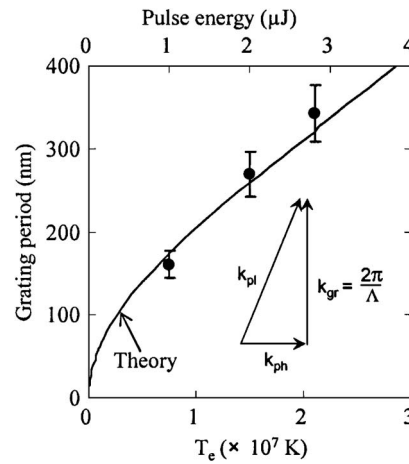
$$\eta_{\text{cr}} = \frac{\omega^2 \epsilon_0 m_e}{e^2}.$$

Another consequence of this model is an energy-dependent nanograting period, which should grow together with pulse energy. For a period of 150 nm induced with 800 nm wavelength ultrashort laser pulses, the following conditions were found: $T_e = 5 \times 10^7$ K and $\eta_e = 1.75 \times 10^{21} \text{ cm}^{-3}$ (Fig. 17). Similar conditions were reported for microexplosions induced with ultrashort laser pulses [121]. However, nanograting formation was observed even for 100 nJ laser pulses, suggesting that nanogratings can also be assembled at subcritical plasma concentrations. Also, electron temperature is limited by the bandgap of the material (for silica glass, electron temperature should not exceed 1.1×10^5 K); hot electrons will dissipate their energy through impact ionization.

Taking these facts into account, the plasmon interference model was modified by assuming two-plasmon decay [28]. The two-plasmon decay is the parametric process in which an incident laser photon splits into two plasmons (two electron plasma waves). The major difference from the previous explanation is the excitation of two bulk plasmons of about half of the photon energy. This parametric process develops when plasma concentration reaches a quarter of the critical:

$$\eta_{\text{TPD}} = \frac{\eta_{\text{cr}}}{4} \sim 4 \times 10^{20} \text{ cm}^{-3}.$$

Figure 17



Nanograting period evolution predicted by plasmon interference theory. Inset shows a wavevector matching diagram. Reprinted from Shimotsuma *et al.* [34].

The interference between two plasmons of the same frequency propagating in opposite directions and satisfying the Cherenkov mechanism of momentum conservation can produce periodic subwavelength modulation. An important signature of two-plasmon decay is the generation of the 3/2 harmonic, which is the result of plasma wave and incident light coupling.

The other attempt to explain the nanograting formation phenomenon was by nanoplasma formation [122]. The idea of this theory is the following. Initially, a focused ultrashort light pulse ionizes defects and color centers, leading to the formation of inhomogeneous plasma [123]. These plasma hot spots, after multiple laser pulses, can evolve into spherically shaped nanoplasma. The local field enhancement at the boundary will result in an asymmetric growth of initially spherical nanoplasma in the direction perpendicular to the laser polarization, where the electric field at the poles E_{pol} and equator E_{eq} of the nanoplasma sphere will be the following:

$$E_{\text{pol}} = \frac{3\epsilon_p E}{\epsilon_p + 2\epsilon_d}, \quad E_{\text{eq}} = \frac{3\epsilon_d E}{\epsilon_p + 2\epsilon_d},$$

where ϵ_d and ϵ_p are the real parts of the electric permittivity for the dielectric medium and plasma. When the electron concentration is below critical, the following condition is satisfied:

$$E_{\text{pol}} < E_{\text{eq}}.$$

The electric field is enhanced at the equator, leading to nanoplane formation. Further evolution of nanoplanes results in quasi-metallic waveguiding, which leads to a prediction of nanograting period equal to $\lambda/2n$, where n is the refractive index of fused silica. This theory encounters difficulties at high electron concentration when $\epsilon_p > \epsilon_d$; as a result $E_{\text{pol}} > E_{\text{eq}}$ and nanoplanes could not be formed [124].

All explanations presented above are related to excitation of plasma and its interaction with light. Some difficulties remain because the plasma frequency

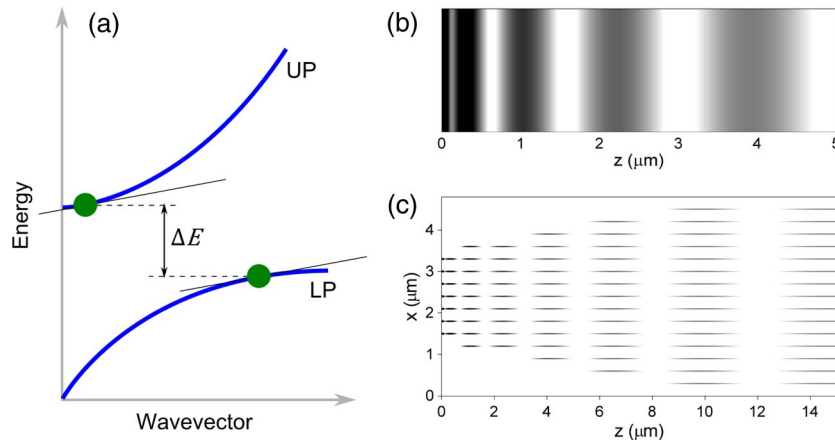
cannot be defined, as it depends on the concentration of free carriers, which is nearly zero in the absence of light and strongly varies as a function of time when the sample is illuminated with a light pulse. It is also unclear how the plasmons may be responsible for the formation of a grating in the propagation direction.

An alternative theory, which is based on attractive interaction and self-trapping of exciton–polaritons, was suggested to explain nanograting formation [125]. It is well known that the absorption spectra of SiO₂ are characterized by a strong exciton peak at about 10.4 eV [126,127]. The binding energy and oscillator strength of excitons in SiO₂ are expected to exceed by orders of magnitude those in GaAs, where excitonic effects are studied in detail. The formation of a polarization grating in the direction of the propagation of light due to interference of exciton–polariton modes in GaAs was predicted more than 11 years ago [128]. The period of this grating was found to gradually increase as a function of the distance from the front edge of the sample due to the dependence of the splitting between two interfering exciton–polariton modes on the group velocity of the exciton–polaritons. In the fused silica case, the two dispersion branches of exciton–polaritons [Fig. 18(a)] may be excited simultaneously by multiphoton absorption. The interference of propagating exciton–polaritons results in formation of the polarization grating (Fig. 18).

The model of exciton–polariton interaction was based on a semiclassical approach. In the direction of light propagation, the excitons were described through the dielectric polarization:

$$\mathbf{P}_{\text{exc}}(z) = \chi_e \mathbf{E}(z),$$

Figure 18



Theoretical simulation of the exciton–polariton interaction in silica glass. (a) A schematic of the exciton–polariton dispersion, showing a point on the upper polariton branch (UP) and a point on the lower polariton branch (LP) with the same group velocity, and their splitting in energy ΔE (not to scale). Panel (c) shows the grating in x and in z , while (b) shows a zoom of the grating in the z direction. In (c), the exciton mean free path is taken as $d = 300$ nm and the exciton mass equal to the free electron mass. Time $t = 300$ fs relative to the arrival of the light pulse at $z = 0$. $\hbar\omega_{\text{LT}} = 0.5$ meV, $\hbar\gamma = 1$ meV, $n_e = 10^5 \text{ cm}^{-1}$, and $\epsilon_b = 3$.

where $\mathbf{E}(z)$ is the electric field, and the dielectric susceptibility of the excitons is given by

$$\chi_e = \frac{\varepsilon_b \omega_{LT}}{\omega_0 - \omega - i\gamma},$$

where ω_0 and ω_{LT} denote the exciton resonance frequency and the exciton longitudinal-transverse splitting, respectively, γ is the exciton nonradiative broadening, and ε_b is the background dielectric constant. The time-dependent polarization was calculated using the scattering state approach in which frequency-dependent solutions of Maxwell's equations (called scattering states) are Fourier integrated with a spectral function characterizing the pulse. The exciton inhomogeneous broadening does not qualitatively change the effect of grating formation [128]. The splitting of exciton-polariton modes in SiO_2 is more than 100 meV, which exceeds the inhomogeneous broadening of the free exciton resonance. The first period of the polariton grating shown in Fig. 18 is very close to the wavelength of light. Then the period increases as a square root of the distance from the sample edge, approximately.

The distribution of excitons in the direction of light polarization was found by describing the system with the Hamiltonian:

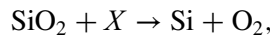
$$H = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \alpha |\psi|^2,$$

where m is the mass of an exciton and α is the negative (attractive) exciton-exciton interaction constant. The Schrödinger equation was solved variationally with a trial function:

$$\psi = \sqrt{\frac{N}{a}} \left(\frac{2}{\pi} \right)^{1/4} e^{-x^2/a^2},$$

where $N = n_{\text{ex}} d$ is the number of excitons, d is the exciton mean free path, and a defines the width of the Gaussian. Then the energy is found and minimized with respect to a .

The lifetime of exciton-polaritons is limited to a fraction of a picosecond (<300 fs) by their phonon-assisted relaxation to indirect states decoupled from light [129]. The indirect excitons can be easily trapped and are essentially immobile and thus can “freeze” the grating pattern formed by exciton-polariton interaction with light [130]. The recombination of the self-trapped excitons is accompanied by the generation of molecular oxygen due to the following reaction [131]:



where X denotes an exciton. Recently, the presence of molecular oxygen was confirmed for GeO_2 glass after femtosecond laser irradiation [132]. Nanopores of silica filled by oxygen are formed in the locations of high concentration of self-trapped excitons. Agglomerations of these nanopores form the nanograting observed in the experiments.

Each of the proposed theories is supported solely by observations made after irradiation. It is not fully clear how nanogratings assembled in matter (while

it is still excited) are imprinted afterward. All of the presented theories consider nanograting formation under single laser pulse irradiation. However, it is well known that nanogratings can be formed only after a sequence of laser pulses. This indicates that some sort of accumulation must take place. Direct experimental observations on nanograting formation would definitely be of benefit to the explanation.

3.7. Physical and Optical Properties of Nanogratings

Femtosecond-laser-induced nanogratings exhibit some curious properties. For instance, they are able to self-replicate over distances much larger than the spot size of the writing beam. Experiments suggest that the structure imprinted earlier provides initial “seeding” conditions during the formation of the self-organized period assembly in the adjacent region [119]. Additionally, nanogratings exhibit extraordinary thermal stability and sustain temperatures of over 1000°C [133]. On the other hand, femtosecond laser pulses with different polarizations can completely overwrite previously modified regions, enabling the exploration of nanogratings as a rewritable optical medium [119,134,135].

The predominant way of characterizing nanogratings is the analysis of the structure under a scanning electron microscope (Fig. 16). Despite its straightforwardness, the method restricts characterization of femtosecond-laser-induced anisotropy to the measurements of the nanograting period. Moreover, it often requires additional postprocessing efforts, such as sample polishing and etching in diluted fluoric acid. The alternative, nondestructive way of characterizing the anisotropic structure is quantitative birefringence measurements, which provide information on the dependence of induced modification on writing parameters such as fluence, repetition rate, and NA [111,136,137].

The effect of form birefringence, unlike intrinsic birefringence, which is due to the anisotropy of oriented molecules, manifests itself due to the alignment of submicroscopic rodlets or platelets [111]. The light polarized parallel to the interfaces experiences a larger refractive index and, as a result, a phase difference for two perpendicular polarizations is acquired. The strength of the birefringence can be controlled by the periodicity and material composition of the microstructure. Under a linear approximation, refractive indices of nanogratings for ordinary n_o and extraordinary n_e wave are

$$n_e = \sqrt{\frac{n_1^2 n_2^2}{f_f n_2^2 + (1-f_f) n_1^2}}, \quad n_o = \sqrt{f_f n_1^2 + (1-f_f) n_2^2},$$

where f_f is the filling factor and n_1 and n_2 are the refractive indices for the platelets constituting the grating. One can see that

$$n_e^2 - n_o^2 = -\frac{f_f(1-f_f)(n_1^2 - n_2^2)^2}{f_f n_2^2 + (1-f_f) n_1^2} \leq 0,$$

i.e., the nanogratings always behave as a negative uniaxial crystal. A typical value of $n_e - n_o$ is $-(2-4 \times 10^{-3})$ [133]. For comparison, quartz crystal is a positive uniaxial crystal and refractive index difference $n_e - n_o = 9 \times 10^{-3}$. It is worth mentioning that aligned rodlets produce positive birefringence [138].

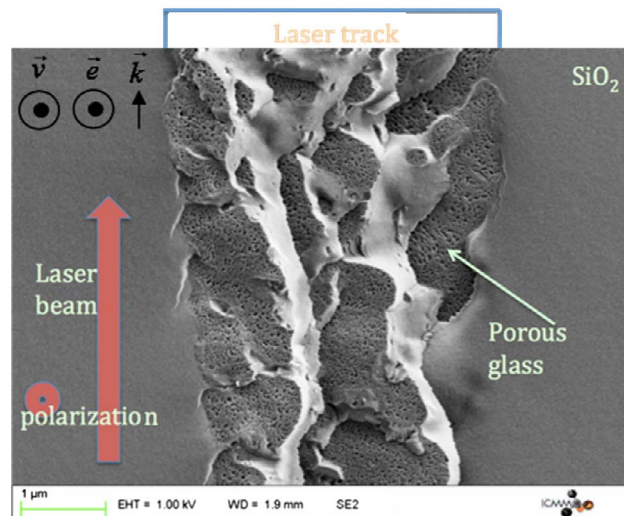
Birefringent modification can be characterized by two parameters: the retardance and the azimuth of the slow axis. On the other hand, they can be independently

controlled during a writing experiment, as the retardance is a function of fluence and the azimuth of the slow axis is defined by polarization.

Observation of birefringence that could be controlled by the polarization of a femtosecond infrared laser beam was first reported by Sudrie *et al.* [113]. It should be noted that in these experiments the femtosecond-laser-induced anisotropy was reported to exhibit positive birefringence. Simultaneously, a peculiar scattering with a propeller-like shape oriented perpendicular to the laser beam polarization was observed in Ge-doped silica glass [112]. It was suggested that aligned subwavelength structures are responsible for this scattering. The experimental observation by Sudrie *et al.* could be explained by the well-known anisotropy due to light-induced anisotropic bond rearrangement (light-induced anisotropy) [139]. Knowing that the nanograting always acts as a negative uniaxial crystal, these experiments do not suggest the presence of a subwavelength structure. However, this could be only an error of sign made in the experiment. All further experiments confirmed the presence of negative birefringence [111]. The discovery of the nanograting produced in the bulk of the material provided an appropriate explanation for both effects [34]. Under certain conditions, this type of glass modification can be an undesirable effect. As revealed from the studies of glass modification dependence on the pulse duration, a smooth refractive index increase cannot be achieved for pulses longer than ~ 200 fs [35]. If waveguides are to be written using relatively long pulses (>200 fs), they potentially can be polarization sensitive and exhibit high propagation losses due to the formation of nanogratings [140]. The problem can be at least partially solved by operating the laser at megahertz repetition rates, where birefringence is strongly reduced due to heat accumulation effects [24,77].

Recent studies indicate that the nanogratings are formed by the alternation of uniform and porous glass layers [131,141] (Fig. 19). The interior of the nanogratings was examined by cleaving the sample after laser irradiation. If

Figure 19



Secondary electron image of the laser-written track after cleaving the sample. Reproduced with permission from Lancry *et al.* [131]. Copyright 2010, Optical Society of America.

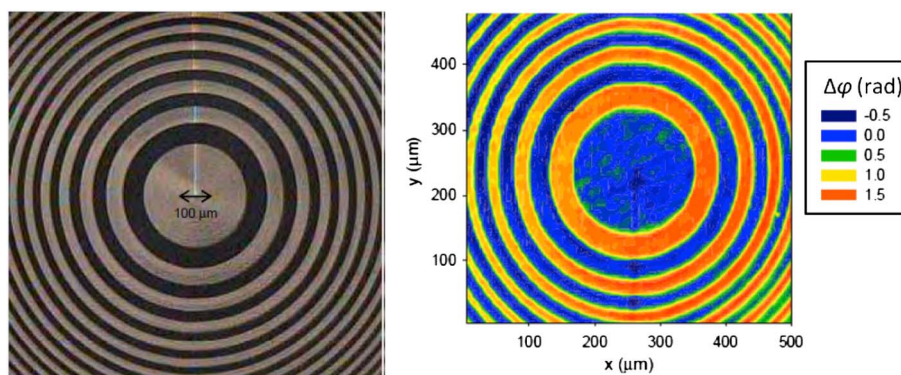
the nanograting planes were parallel to the cleavage, the interior structure could be observed with a field emission electron microscope, which revealed small features otherwise covered by conductive coating. The formation of nanopores is attributed to SiO_2 decomposition into $\text{SiO}_{2(1-x)} + x \cdot \text{O}_2$ under intense laser irradiation. The typical diameter of nanopores ranges from 10 to 30 nm. Small angle x-ray scattering measurements further confirmed the nanoporous structure of the nanograting interior [141].

3.8. Applications of Femtosecond-Laser-Induced Nanogratings

The peculiar optical properties of femtosecond-laser-induced nanogratings allowed implementation of numerous optical elements with various functionalities. Unknowingly, the first diffractive optical element, the Fresnel zone plate, was fabricated in the nanograting formation regime [142] (Fig. 20). Nanogratings exhibit much larger refractive index change than isotropic refractive index increase. For diffractive optics, the sign of the refractive index does not play a crucial role; thus, a negative refractive index change of nanogratings is well suited for this purpose. To fabricate a Fresnel zone plate, it is necessary to induce a phase retardation of π between odd and even numbered Fresnel zones. This can be achieved either by modulating the thickness of the material or by modifying the index change. The femtosecond laser was used to induce refractive index change in the odd numbered Fresnel rings. The radius of the fabricated zone plate was 1 mm, and, with 158 zones, it was designed to focus light with wavelength of 632.8 nm at a distance of 1 cm. In the crossed polarizers, the modified areas became bright, clearly indicating that the laser induced the birefringent modification. Measurements of the phase shift revealed that the laser-induced modification exhibited negative refractive index change. Also, phase retardation for the designed wavelength induced by a single laser scan was not π but rather $\pi/2$. An efficient zone plate thus requires multiple scanning or different focusing conditions.

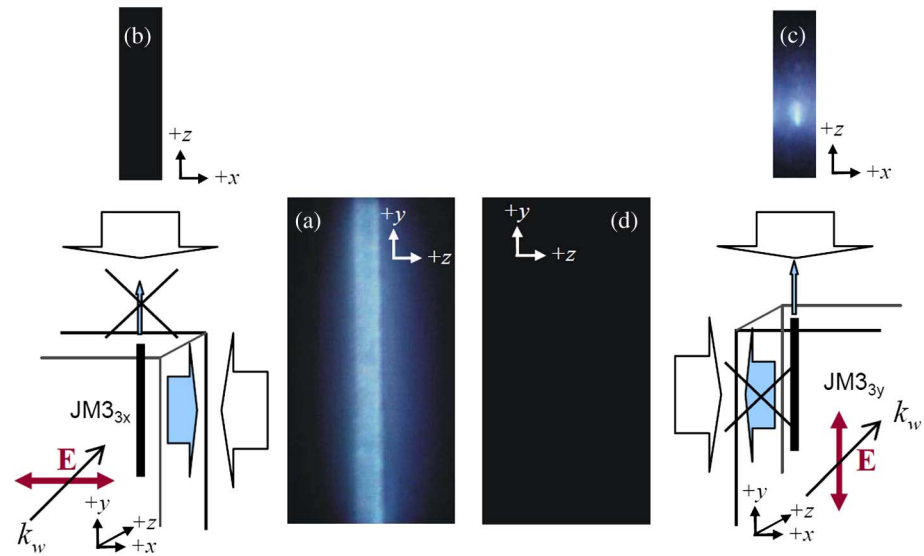
Another interesting observation was anisotropic reflection [144], which at that time hinted at the presence of subwavelength nanostructures. In the

Figure 20



(Left) Microscope image of the central part of the Fresnel zone plate in the cross-polarized light. (Right) Phase retardation $\Delta\phi$ of the zone plate measured with the interferometric setup. Reproduced with permission from Bricchi [143].

Figure 21

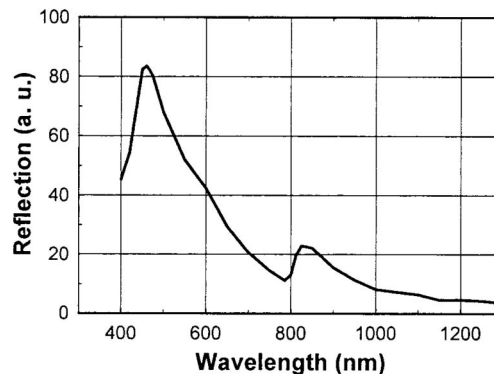


CCD camera images of the reflection from laser-written tracks. The red arrows indicate the orientation of the polarization of the writing beam. The strong reflection is observed only along the electric field direction. Reproduced with permission from Bricchi [143].

experiment, a series of diffraction gratings were written in the fused silica sample. After irradiation, the modified areas were inspected through the silica plate's polished edges with an optical microscope. During the inspection, the structures were illuminated with unpolarized white light. Unexpectedly, striking reflection in the blue region of spectrum was observed (Fig. 21). Spectral analysis revealed that the reflected light exhibited two peaks: the strongest one at 460 nm, which explains the blue character of the reflection, and a weaker one at 835 nm (Fig. 22).

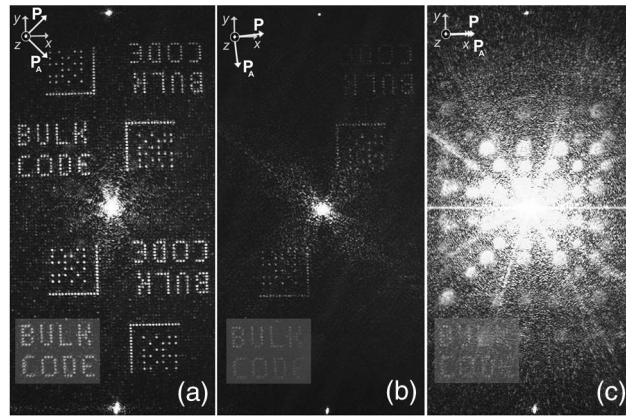
A more detailed study revealed that the reflection occurred only when the viewing axis was parallel to the electric field vector and the energy per pulse was above a certain threshold. The blue reflection was observed only for

Figure 22



Spectrum of the light reflected from a laser-inscribed track. Two peaks can be explained by refractive index modulation with a period of 150 nm. Reprinted from Mills *et al.* [144].

Figure 23



Reconstruction of a CGH. The highlighted areas were used for measuring the signal-to-noise ratio. $\mathbf{P}$, input beam polarization; $\mathbf{P}_A$, analyzer direction. (a) Reconstruction under crossed polarizers with input polarization at $\theta = 45^\circ$, (b) reconstruction under crossed polarizers with input polarization at $\theta = 2^\circ$, and (c) reconstruction with parallel polarizers at 0° . Reproduced with permission from Papazoglou and Loulakis [145]. Copyright 2006, Optical Society of America.

birefringent modifications, indicating that the two phenomena are related. Indeed, the peak at 460 nm can be explained by the Bragg reflection from a modulation of refractive index with a period of 150 nm. Later on, this assumption was confirmed by Shimotsuma *et al.* [34].

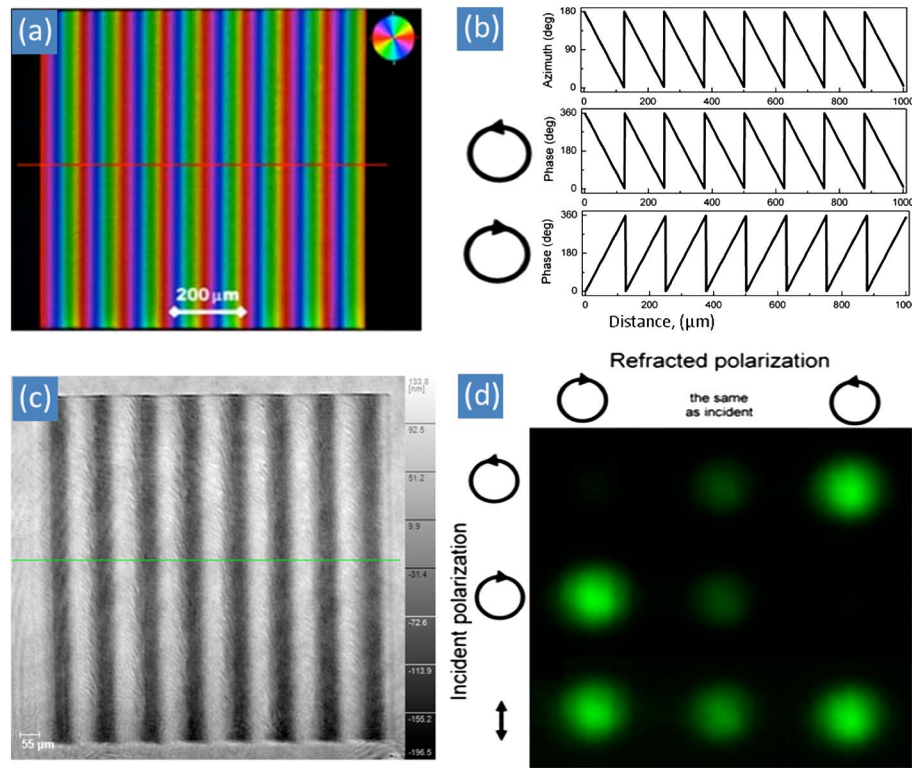
Recently, several polarization-sensitive optical elements were implemented to explore the birefringent properties of nanogratings. The laser-structured area behaves as a waveplate of the size of a few micrometers. The parameters of the waveplate, retardance, and orientation are controlled by the pulse energy and polarization. Using lenses of moderate NA (0.15–0.2), the optical elements with half-wave retardance for ~ 500 nm can be written in a single scan at a speed of several millimeters per second. Several groups demonstrated computer-generated holograms (CGHs) printed with self-assembled nanogratings [145,146] (Fig. 23). The birefringence exhibited by nanogratings allows a significant increase in the signal-to-noise ratio, of at least 9 dB, by polarization filtering, which suppresses the undiffracted beam.

The first element that was demonstrated was a polarization diffraction grating [147]. Instead of continuous phase or amplitude modulation, a polarization grating is imprinted in slow axis modulation (Fig. 24). The efficiency of this diffraction grating depends directly on the induced retardance [148]. The highest efficiency is at half-wave retardance, and then all incident energy is distributed between the -1 and 1 diffraction orders. The effect of the spatially variant half-wave plate on the circular polarization can be described using Jones matrix formalism:

$$\begin{pmatrix} \cos(2\theta) & \sin(2\theta) \\ \sin(2\theta) & -\cos(2\theta) \end{pmatrix} \begin{pmatrix} 1 \\ i \end{pmatrix} = e^{2\theta i} \begin{pmatrix} 1 \\ -i \end{pmatrix},$$

$$\begin{pmatrix} \cos(2\theta) & \sin(2\theta) \\ \sin(2\theta) & -\cos(2\theta) \end{pmatrix} \begin{pmatrix} 1 \\ -i \end{pmatrix} = e^{-2\theta i} \begin{pmatrix} 1 \\ i \end{pmatrix}.$$

Figure 24

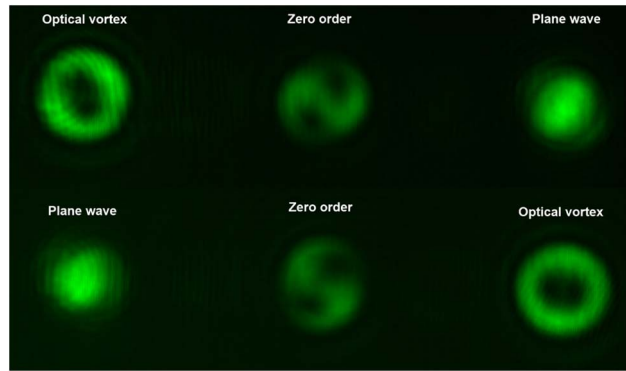


(a) Microscope image where pseudo colors indicate the direction of the slow axis in the polarization diffraction grating. (b) Slow axis orientation and the corresponding phase modulation for two circular polarizations across the red horizontal line indicated in (a). The direction of the phase grating depends on the handedness of the circular polarization. (c) Gray-scale map of birefringent grating phase variation measured with a digital holography microscope for linear polarization. (d) Far-field diffraction images for the incident right/left-handed circular and linear polarizations.

The Jones matrix operator on the left-hand side of the equation represents a half-wave plate, and the vector indicates circular polarization $[(1, i), \text{left-handed}; (1, -i), \text{right-handed}]$. After a half-wave plate, the polarization changes its handedness and acquires phase retardation equal to $\pm 2\theta$, where θ is the angle of the wave plate slow axis. One can notice that the sign before the phase factor 2θ depends on the handedness on the polarization. As a result, the same half-wave plate grating with slow axis modulation [Fig. 24(a)] will have different phase modulation depending on the handedness of the polarization [Fig. 24(b)]. Thus the polarization diffraction grating will exhibit selectivity for the circular polarization, as is observed in the experiment. Depending on the polarization handedness, the laser beam is diffracted to the -1 or 1 diffraction order [Fig. 24(c)]. Effectively, the polarization diffraction grating operates as a circular polarization beam splitter.

An interesting effect can be observed if spatially variant polarizations, which will be discussed later in this text, are incident on this diffraction grating. The incident radial or azimuthally polarized optical vortex is decomposed into

Figure 25

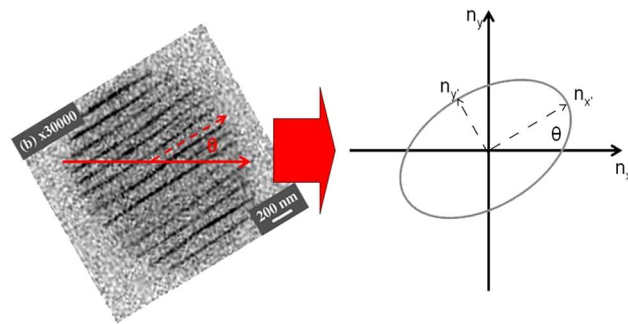


Radially/azimuthally polarized optical vortex split by a polarization diffraction grating into two circularly polarized waves of opposite handedness: plane wave and optical vortex.

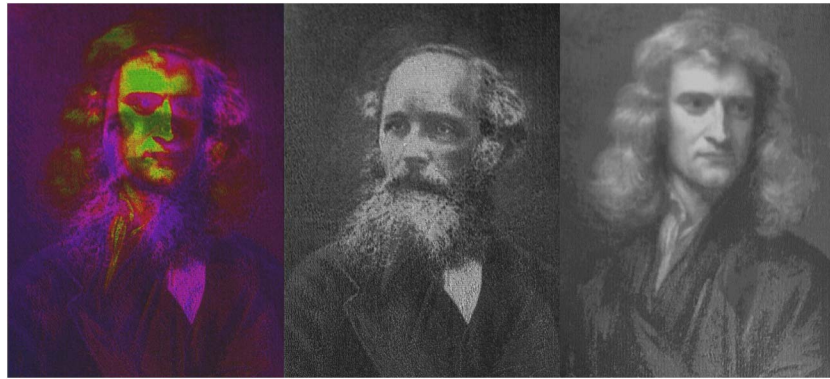
a circularly polarized plane wave and an optical vortex with angular momentum $l = 2$ (Fig. 25).

As was mentioned above, laser-induced anisotropy can be characterized by two independent parameters: retardance and slow axis orientation, which can be rewritten with successive pulse sequences (Fig. 26). Recently, it was proposed that by using these parameters, optical recording can be extended beyond the three spatial dimensions [125,135]. The nanograting's ability to withstand temperatures of 1000°C makes nanostructure-based memory ideal for archiving a large volume of important information. The ability to record and read several layers of information via nanogratings was demonstrated by Shimotsuma *et al.* [135]. During the recording procedure, the number of pulses and the azimuth of their polarizations can independently control induced retardance and slow axis direction [125]. The retardance can be controlled with a precision of about 10 nm, while slow axis angle can be defined with a few degrees precision. The read-out procedure was demonstrated with the quantitative birefringence measurement system Abrio (CRi Inc.), which can measure the two parameters with a precision of less than 1 nm and 1 deg, respectively. The ability to record data simultaneously in retardance and the slow axis direction was demonstrated by Beresna *et al.* [125]. Portraits of two prominent scientists, James Clerk Maxwell

Figure 26



Schematic description of two parameters describing birefringence: slow axis angle θ and retardance $(n_x' - n_y') \cdot d$.



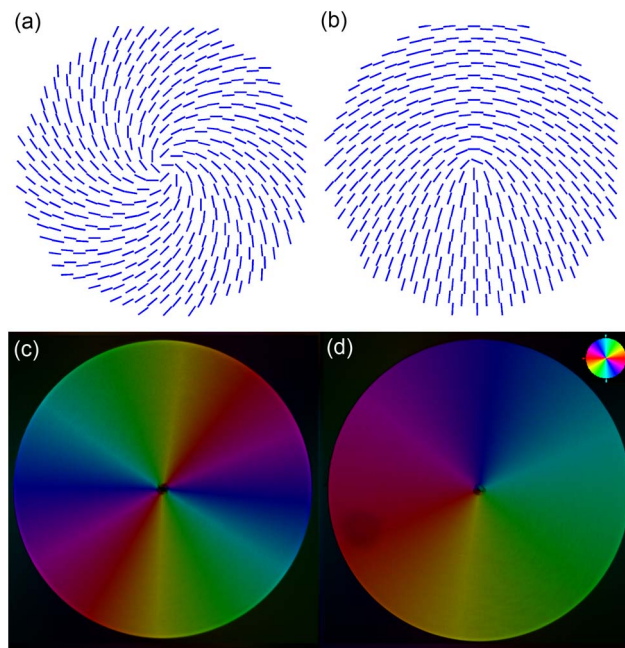
(Left) Abrio image representing in false colors the recorded information in slow axis and retardance. (Middle and right) Decoupled images of Maxwell and Newton (no additional operations on images were performed). Reprinted from Beresna *et al.* [125].

and Isaac Newton, were recorded in the same physical birefringent layer. For encoding, the two gray-scale (256 gray levels) portraits were first matched in pixel size. The Newton portrait was then split into eight layers and combined with an image of Maxwell using a MATLAB code. Finally, eight gray-scale images were generated and each was recorded with a different polarization orientation by varying the number of pulses with respect to the pixels' gray-level value. As a result, the portrait of Maxwell was encoded in retardance and Newton's image was recorded in the variation of slow axis orientation. Using the Abrio microscope system, the two images were successfully decoupled, clearly demonstrating the potential of the proposed information recording technique (Fig. 27).

Another application of femtosecond-laser-induced nanogratings is polarization converters. Typically in optics, only two states of polarization are discussed: linear and circular. Both polarization states are spatially homogeneous, i.e., in every part of the light beam the polarization state is the same. However, increasing interest has recently arisen in the spatially variant polarization states. Those most examined are radial and azimuthal polarizations [149]. Recently, beams with such polarizations have been actively investigated for the unique properties they exhibit under focusing at high NAs. Numerical calculations have shown that tighter focus can be obtained using radially polarized annular beams, which results from the strong and localized longitudinal electric field [150,151]. This effect has been experimentally confirmed by several groups [152,153] and has already found applications in high-resolution imaging, such as nonlinear microscopy [154,155] and dark-field imaging [156]. Additionally, radial polarization is ideally suited for exciting surface plasmons, which require p -polarized light, in axially symmetric optical systems [157]. Large longitudinal electric fields generated with radially polarized beams have also been explored for particle acceleration [158].

The main hindrance to widespread use of such polarization modes is the lack of simple and cost-effective ways to generate them. The symmetric polarization states are also very sensitive to any phase distortion, which can be introduced, for instance, by a reflection from a dielectric mirror. As a result, spatially variant polarization should be generated just before the focusing optics. Thus,

Figure 28

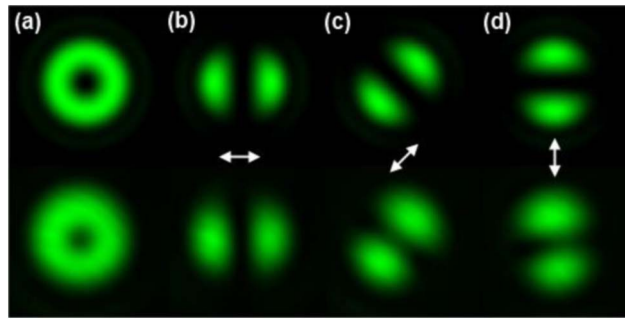


Schematic drawings of nanograting distribution in (a) quarter- and (b) half-wave polarization converters. Femtosecond-laser-written radial polarization converters for (c) circular and (d) linear incident polarizations. The pseudo color indicates direction of the slow axis. Reprinted from Beresna *et al.* [159].

polarization generation should not only be efficient but also provide a compact setup. In this respect, the nanogratings induced by femtosecond laser irradiation are a perfect choice for polarization converters operating in the visible and near-infrared. In the experiments, structures with birefringence of up to 200–300 nm can be written by focusing a laser beam with NA from 0.1 to 0.2 [159]. Higher retardance can be achieved by stacking several layers together [136]. The writing speed can be up to several millimeters per second, enabling coverage of several square millimeters in several hours. Laser-induced form birefringence not only allows writing permanent quarter- or half-wave plates but also fabricating spatially variant birefringent elements [137,159,160] (Fig. 28). One such birefringent device is the radial polarization converter or s-wave plate (“s” stands for “superstructured”). The s-wave plate can be made in two different configurations depending on its function. The quarter-wave plate generates a radially polarized optical vortex upon incident circular polarization. The vortex charge depends on the handedness of incident polarization. The half-wave plate can have two different functions.

If linear polarization is incident, then on the output, radial or azimuthal polarization can be produced (Fig. 29), while for incident circular polarization, the converter produces a circularly polarized optical vortex. Both types of converter were successfully implemented for visible and infrared wavelengths. The demonstrated polarization converters provide a convenient extracavity method, obtaining spatially variant polarization states. A high damage threshold of laser written structures enables using these elements for material processing, such as sheet metal cutting or transparent material ablation [161–163].

Figure 29



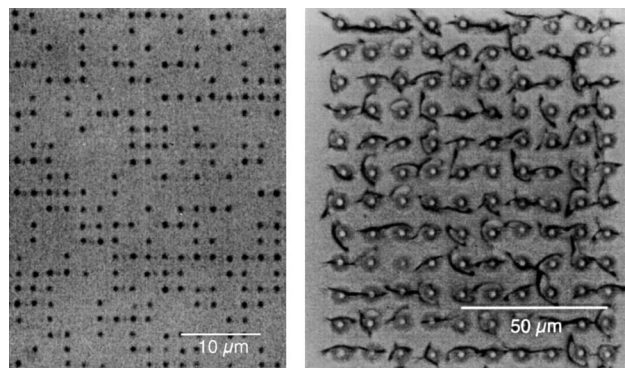
Modeled (top) and measured (bottom) profiles of generated radial polarization directly (a) after a converter and (b)–(d) after a polarizer. The white arrows indicate the transmission axis of the polarizer inserted between the converter and the CCD camera. Reprinted from Beresna *et al.* [159].

3.9. Bubbles

The third type of modification is bubbles, which were observed in several different situations and exhibited different character.

The first demonstration of femtosecond-laser-induced bubbles dates back to 1996, when ultrafast laser direct writing was suggested for three-dimensional optical storage [7]. Voids of 1 μm with densified material in the vicinity were written with 0.5 μJ of energy focusing 100 fs, 780 nm pulses with a 0.65 NA objective. Formation of these voids was attributed to microexplosion, which is a result of high temperatures and pressure ejecting material from the center into the surrounding volume. Despite redistribution of the material, the surrounding media did not exhibit any cracking, as opposed to picosecond and nanosecond pulses (Fig. 30). A more thorough study demonstrated that voids of 200–250 nm can be induced in multiple transparent materials, such as fused silica, quartz, and sapphire [121]. In sapphire, the estimated values of pressure were from 1700 to 3000 GPa. Another group predicted pressures up to 10 TPa and temperatures of 5×10^5 K induced by femtosecond laser irradiation in

Figure 30

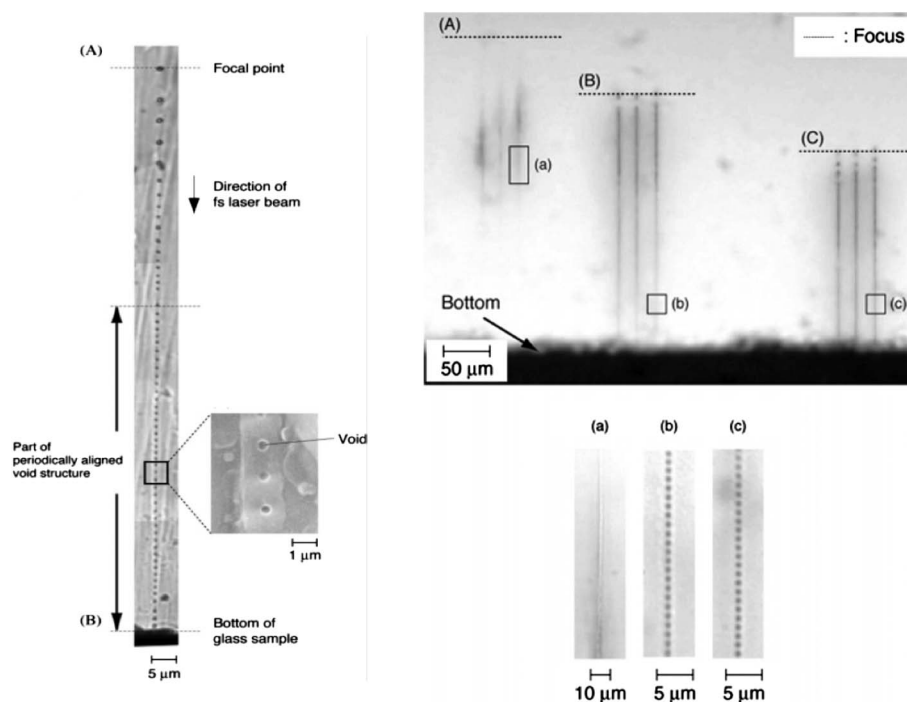


Array of dots written with 100 fs laser pulses (left) and an array written with 200 ps laser pulses (right). Reproduced with permission from Glezer *et al.* [7]. Copyright 1996, Optical Society of America.

sapphire [66]. The subwavelength size of the voids was first explained by self-focusing of the laser to a waist diameter of 150 nm [121]. However, this prediction neglected plasma defocusing. Also, later studies demonstrated that similar voids can be induced below the self-focusing threshold [164].

In certain situations laser irradiation can induce a chain of well-organized bubbles [165–168]. Several groups have proposed different explanations for this phenomenon. One explanation was based on an analogy to a fiber fuse, where damage propagates from the surface toward the laser beam [165]. The laser beam heats the surface and a void occurs close to it, as the damage on the surface is lower than inside the bulk. The next femtosecond pulse will start heating the vicinity of the newly formed void, resulting in subsequent void formation. In this closed-loop situation, the void chain will progress toward the laser beam. This suggestion was supported by experiments in which 10–40 μJ 120 fs laser pulses were focused with a 0.9 NA microscope objective into borosilicate glass. High energy led to the formation of filament, which produced an extended channel-like modification. Filament formation could also be assisted by spherical aberrations, which should be definitely present at such high-NA and deep-focusing conditions. If the modification reached the exit surface of the sample, a chain of bubbles was produced. However, this effect occurs only if the laser is focused close to the exit surface of the sample (Fig. 31).

Figure 31



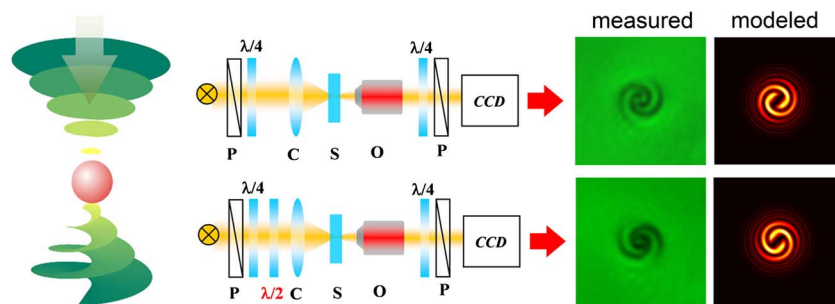
(Left) Cross section of the 0.9 mm thick borosilicate glass after irradiation with a 10 μJ femtosecond laser beam at a 1 kHz repetition rate for 0.25 s. The focus was 750 μm below the entrance surface. (Right) Cross section of the glass sample after the laser exposure for 1 s (1000 pulses) focused at depths of (A) 750 μm , (B) 860 μm , and (C) 940 μm from the entrance surface. The dotted lines indicate the focal planes of the laser beam. Enlargements of parts of (a)–(c) are shown below. Reprinted with permission from Kanehira *et al.*, Nano Lett. **5**, 1591–1595 (2005) [165]. Copyright 2005 American Chemical Society.

However, periodic bubble formation was also observed far away from the exit surface. The experiments were also performed with a 0.9 NA objective, which focused a laser beam several hundreds of micrometers into the bulk of fused silica [166]. As opposed to Kanehira's experiments, in this case a chain of bubbles with gradually decreasing size was formed. The explanation was based on spherical aberrations, which were shown to produce quasi-periodic intensity modulation. However, the modeling was performed in the linear regime, and electron plasma was strongly affecting the propagation of light. The bubble formation was also explained in the multiple pulse regime. It was shown that a single pulse does not produce a bubble chain; instead, there appears a long smooth channel [168]. After several successive pulses the bubble chain evolved, which was explained as a result of the smooth channel's collapse.

An interesting effect of spin-to-orbital momentum coupling was observed on laser-induced bubbles in fused silica [167]. The incident circular polarization could partially acquire angular momentum being scattered by an embedded bubble. The sign of the angular momentum could be controlled by the handedness of incident circular polarization (Fig. 32). The effect was explained by polarization-dependent Fresnel reflection from a cylindrically symmetric interface between the bubble and the glass. The p -polarized light has a higher transmission coefficient and, as a result, part of the incident circularly polarized light becomes radially polarized. Additionally, this radially polarized light acquires orbital angular momentum, resulting in a radially polarized optical vortex.

Another type of bubble formation was observed at a high repetition rate [23]. The experiments were performed at a 10 MHz repetition rate in silica and borosilicate glasses. As was mentioned before, in the megahertz regime, heat accumulation strongly affects material modification. With the increase of the pulse energy above a certain threshold, the continuous isotropic modification turns into a chain of self-organized bubbles, which was called a "pearl-chain." The period of the bubbles was varying only within 5% and showed very weak dependence on writing speed. The cross section of the modification reveals a

Figure 32



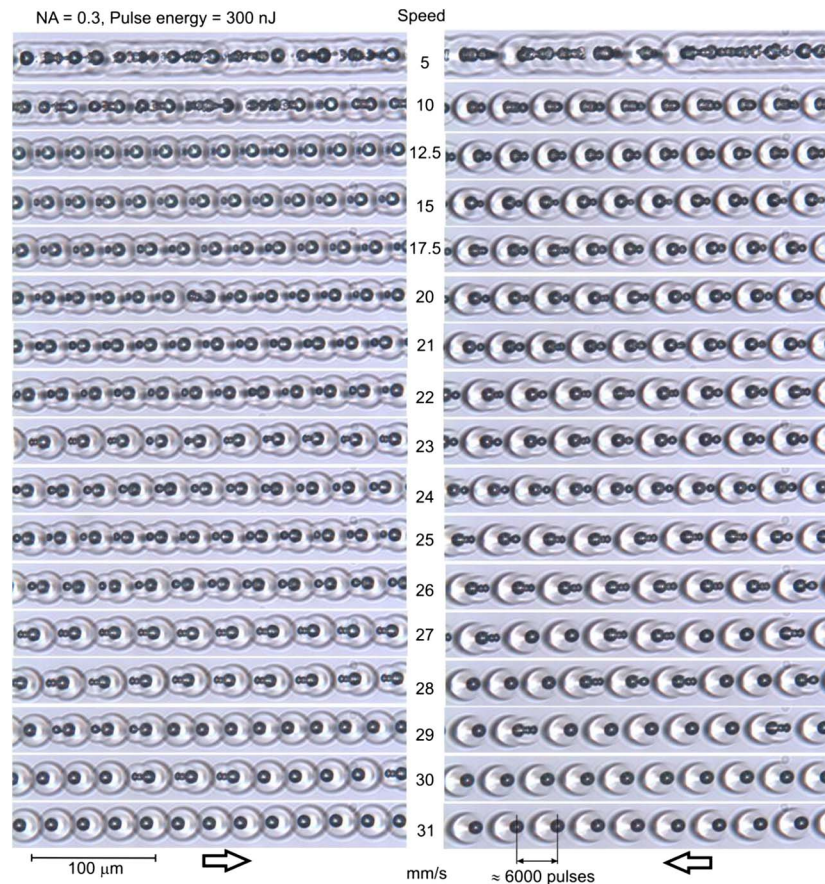
(Left) Optical vortex generation on an isotropic sphere. Incident circularly polarized light with plane front ($l = 0$) after refraction on a spherical surface is partially converted into an optical vortex with orbital angular momentum $l = 2\hbar$. (Right) Optical setups for optical vortex observation. P, polarizer; C, condenser; S, sample; O, objective. Vortex patterns (measured and modeled), observed under left- and right-handed polarizations, show mirror symmetry, indicating reverse of the orbital momentum sign. Reprinted from Beresna *et al.* [167].

complex inner structure, where several groups of bubbles are formed in the volume of modified material. The self-organized structure even exhibited light-guiding properties with optical losses of 6 dB/cm at 1.5 μm .

Another recent study demonstrated transition from chaotic to organized bubble formation [169]. In these experiments, the writing speed was gradually increased from 5 to 30 mm/s while maintaining the pulse energy constant (Fig. 33). At low speed, the modification appears erratic. Only above 10 mm/s do self-organized patterns with variable complexity and periodicity emerge. Well-separated bubbles similar to the pearl-chain-type modification have been observed above 30 mm/s.

The bubble formation in this case is a result of multiple pulse irradiation. If the temperature of the glass due to heat accumulation reaches critical temperature, rapid bubble nucleation is triggered. Bubble formation, however, distorts the laser beam at the focus, effectively switching off the heat source and stopping further bubble nucleation. When the laser beam moves out of the modified region, the process of glass heating and bubble formation starts again. This process

Figure 33



Transition from chaos to order. The pattern of bubbles depends on the writing speed. The tracks were written with the same pulse energy (300 nJ) at a 9.4 MHz repetition rate. The bubble pattern also depends on the writing direction (indicated by arrows at the bottom of the image). Reproduced with permission from Bellouard and Hongler [169]. Copyright 2011, The Optical Society of America.

was illustrated by an analogy to a siphon, which allowed demonstration of not only bubble chain formation but also the transition from erratic to organized process.

Interestingly, despite the high stability of periodicity, defined by writing speed and energy, the authors also observed a directional dependence, where the character of the modification depends on the direction of writing, similar to the quill effect discussed earlier [85].

4. Conclusions

In this paper we have reviewed the progress in the field of ultrafast laser direct writing, which has rapidly developed from the initial scientific studies to commercially viable technology. Over two decades this field has grown enormously. We did not attempt to include everything in the scope of this review; we mainly concentrated on modification of transparent materials and did not touch on such topics as processing of metals, semiconductors, or polymers, which are vast and active areas of femtosecond laser processing.

From the very beginning, this field was strongly influenced by the development of ultrafast laser systems, which is, in fact, the key part of the ultrafast laser direct writing setup. For example, the initial demonstration of waveguide writing was implemented after introducing Ti:sapphire laser systems with high operation stability. Thus, future trends in this field should also be determined by the evolution of femtosecond laser systems. We can already see that high average power femtosecond laser systems operating at more than 100 W opened doors to industrial-scale applications, where requirements are raised not only for quality but also for the speed of the process [170–172]. Several commercial systems based on compact and reliable fiber lasers were introduced for two-photon polymerization and glass processing.

The flexibility of this technique in terms of materials and ability to implement 3D geometries with subwavelength precision turned it into an ideal low-cost platform for rapid prototyping, which was explored in the fields of microfluidics, quantum optics, etc.

For industrial applications, the implementation of parallel processing in ultrafast laser direct writing is of crucial importance. Commonly, even nanojoule laser pulses can modify the material; however, conventional focusing techniques do not allow exploration of the whole power capacity of a laser system. Adding adaptive optics elements into the laser direct writing system has already demonstrated the potential of process parallelization, increasing writing speed, and reducing production cost.

Several areas of femtosecond laser processing, including laser assisted etching and self-assembled nanostructuring, have evolved into self-contained fields of research, with a rapidly growing number of applications.

The combination of short pulse duration and broad spectrum requires more subtle control of dispersion in ultrafast pulse delivery systems. On the other hand, this challenge opens new opportunities for direct writing with tailored laser pulses.

The theoretical aspects of the interaction of ultrashort pulses with matter still require major advancements. Although experimentally the spatiotemporal

effects can be easily observed, the mechanisms of interaction of matter with laser pulses shaped in space and time remain unclear.

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